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BARIUM AND RADIUM IN WATER TREATMENT PLANT WASTES

by

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16. ABSTRACT

Water treatment plants at nine locations (10 plants) in Illinois and Iowa were studied to determine the characteristics and disposal practices for the sludge, brine, and backwash water containing radium (Ra) and/or barium (Ba). The treatment processes in these ten plants include iron (Fe) and manganese (Mn) removal (3 plants), lime softening (4 plants), and ion exchange (3 plants). Eight plants had radium and three plants had barium. The data are needed to determine whether special procedures are required to dispose of such wastes.

Influent Ra^{226} concentrations for the eight plants that were studied ranged from 0.3 to 49 pCi/L. Radium removal averaged 8%, 75%, and 85% for Fe and Mn, lime softening, and ion exchange respectively. Theoretically, the amount of radium removed estimates the quantity of radium in the waste. The data showed that backwash water from Fe and Mn removal plants contained average Ra^{226} concentrations that ranged from 21.2 to 106 pCi/L and average Ra^{228} concentrations ranged from 5.7 to 20 pCi/L. Lime softening sludge, on a dry weight basis, ranged from < 1.2 to 21.6 pCiR^{226}/g and from < 2.4 to 11.7 pCiRa^{228}/g. Ion exchange plant brine contained peak Ra^{226} concentrations of 217 and 1,144 pCi/L.

Influent barium concentrations for the three plants studied ranged from 4.0 to 16.1 mg/L. Lime softening and ion exchange removed barium to concentrations that were below the MCL of 1.0 mg/L. Barium removal during lime softening is pH dependent. Theoretically, the amount of barium removed estimates the quantity of barium in the waste. Barium concentrations in the brine from two ion exchange plants that were tested, averaged 328 and 1,297 mg/L. Peak concentrations of barium from the two brines were 1,197 mg/L and 5,161 mg/L.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the research and the user community.

This study was undertaken to determine the concentrations of barium and radium in water treatment plant wastes. These data are needed to establish whether special procedures are required to dispose of such wastes. Samples from several water plants in Illinois and Iowa were analyzed for these substances, and the values obtained were compared to those that have been reported in the literature.

ABSTRACT

Water treatment plants at nine locations (10 plants) in Illinois and Iowa were studied to determine the characteristics and disposal practices for the sludge, brine, and backwash water containing radium (Ra) and/or barium (Ba). The treatment processes in these ten plants include iron (Fe) and manganese (Mn) removal (3 plants), lime softening (4 plants), and ion exchange (3 plants). Eight plants had radium and three plants had barium. The data are needed to determine whether special procedures are required to dispose of such wastes.

Influent Ra^{226} concentrations for the eight plants that were studied ranged from 0.3 to 49 pCi/L. Radium removal averaged 8%, 75%, and 85% for Fe and Mn, lime softening, and ion exchange respectively. Theoretically, the amount of radium removed estimates the quantity of radium in the waste. The data showed that backwash water from Fe and Mn removal plants contained average Ra^{226} concentrations that ranged from 21.2 to 106 pCi/L and average Ra^{228} concentrations ranged from 5.7 to 20 pCi/L. Lime softening sludge, on a dry weight basis, ranged from < 1.2 to 21.6 $pCiRa^{226}/g$ and from <2.4 to 11.7 $pCiRa^{228}/g$. Ion exchange plant brine contained peak Ra^{226} concentrations of 217 and 1,144 pCi/L.

Influent barium concentrations for the three plants studied ranged from 4.0 to 16.1 mg/L. Lime softening and ion exchange removed barium to concentrations that were below the MCL of 1.0 mg/L. Barium removal during lime softening is pH dependent. Theoretically, the amount of barium removed estimates the quantity of barium in the waste. Barium concentrations in the brine and rinsewater from two ion exchange plants that were tested, averaged 328 and 1,297 mg/L. Peak concentrations of barium from the two brines were 1,197 mg/L and 5,161 mg/L.

Disposal processes that were used, for the plants that were studied, were lagooning, discharge to sanitary sewers and discharge to a water course.

This report was submitted in fulfillment of Contract No. CR-808912 by the University of Illinois at Urbana-Champaign under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 1, 1983 to December 31, 1983, and work was completed as of April 1984.

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SECTION 1

INTRODUCTION AND OBJECTIVES

Naturally occurring barium (Ba) in drinking water exceeds the maximum contaminant level (MCL) of 1 mg/L in some areas of northern Illinois and northeastern Iowa. In these same areas and in some parts of Florida, the concentrations of radium^{226} (Ra^{226}) plus radium^{228} (Ra^{228}) exceed the MCL, which is 5 pico-Curies (pCi)/L. Most of the contaminated supplies are used by small communities, many of which do not presently treat their water to reduce the concentrations of these substances. Both Ra and Ba are alkaline earth metals, and both are found in water as divalent cations. Their chemical behavior is very similar, and it is much like that of calcium (Ca^{2+}) and magnesium (Mg^{2+}), the principal components of hardness in water. The MCL's for Ba and Ra were developed to minimize the attack of these elements on human bones and the replacement of the Ca in bones. Their similarity to Ca, however, means that processes used to soften water are also very useful for removing these contaminants from drinking water.

Water treatment in small communities is often accomplished with iron and manganese (Fe and Mn) removal plants, lime softening plants, and ion exchange plants. The objective of this research was to characterize the backwash samples from all three types of plants, as well as the sludges from the lime softening plants and the brines from ion exchange plants. Table 1 lists the plants studied and the populations they served. The concentration data were needed to determine whether special procedures are required to dispose of such wastes. The Ba and Ra removal efficiencies of the plants were also determined.

Table 1

Type and Location of Water Treatment Plants

Softening Plants	*Population
Colchester, IL	1,700
Elgin, IL	25,000**
Bushnell, IL	3,800
West Des Moines, IA	21,900
Ion Exchange Plants	
Crystal Lake, IL	18,600
Eldon, IA	1,300
Filtration Plant	
Adair, IA	900
Stuart, IA	1,700
Table Grove, IL	<500

* From Rand McNally Road Atlas, 1983
** Population of the community is 63,800

SECTION 2

CONCLUSIONS

Ion exchange plants, lime softening plants, and iron and manganese removal plants can remove radium from water with varying degrees of success. The iron and manganese treatment plants removed 0% to 54% of the influent radium, which ranged in concentration from 6.0 to 49 pCi/L. This study indicated that the lower percent removals were more common. The average removal, including values taken from the literature, was 23%, but the mean for this study was only 8%. The total radium content of the waters from a single backwash was 0.02 to 7.6 μCi, and concentrations were typically less than 100 pCi/L. The average radium removal by the plants was 11%, as indicated by analysis of backwash water concentrations. Though a relationship between MnO_2 accumulation on the filters and radium removal was expected, sufficient data were not available to show this relationship. Treatment methods such as lime softening or ion exchange seem better suited than iron and manganese removal plants for removing radium from water supplies.

Lime softening does effectively remove radium from waters. The influent concentrations were 0.3 to 24.2 pCi/L. Typical removal values ranged from 43% to 92%, with an average of 69%, if data from the literature are included. The radium removal at the plants sampled during the summer varied from 45% to 78%, with an average of 75%. The quantity of radium removed is a good estimate of the quantity of radium in the sludge. Two correlations presented in the paper relate hardness removal to radium removal and can be used to predict radium removal efficiencies. The radium concentrations in the softening sludges ranged from <1.2 to 21.6 pCi/g dry solids for radium ^{226} and from <2.4 to 11.7 pCi/g dry solids for radium ^{228}. Lagooning and discharge to sanitary sewers were used as disposal methods.

Ion exchange plants also produce an effluent with low radium concentrations. The plant at Eldon removed 60% of the influent radium of 47 pCi/L but insufficient regenerant was applied. Common removals reported in the literature are 65% to 90% while the average removal approaches 85%. The radium removed is also that expected in the brine. The radium concentration in two brines at Eldon were 217 pCi/L and 1,144 pCi/L, and higher concentrations at other locations were reported in the literature. In some areas, the discharge of brines to a water course is not prohibited; this method was employed at Eldon.

Ion exchange and lime softening plants were also analyzed for barium removal. Crystal Lake (ion exchange) removed more than 90% of the influent 9.5 and 16.1 mg/L of barium. The barium concentrations in the brine at Wells 6 and 8 averaged 328 and 1,300 mg/L, with peak values of 1,200 and 5,200 mg/L, respectively. The total quantity of barium in the brine should be approximately the same as was removed during the run. The spent brine is discharged to the sewer. Lime softening at Elgin also removed 90% of the 4 mg/L barium in the influent water. Unfortunately, little information is available on procedures that can be used to dispose of wastes containing barium.

SECTION 3

MATERIALS AND METHODS

The samples were collected before and after the processes that were likely to cause a change in radium or barium concentration. Samples were taken from lagoons, clarifier sludges, and backwash waters whenever available. Samples were also taken every five minutes during regeneration at the ion exchange plants. Each sample was collected in two 500-mL polyethylene bottles, and an additional 1-L samples was taken if the sample was to be analyzed for radium. With the exception of the chloride, barium, and radium analyses, all of the samples were tested within 1 week (and usually within 2 days).

The samples were tested for total alkalinity, total dissolved solids, pH, total hardness, calcium, chloride, barium, and radium (if present). Standard Methods (1) outlines the procedures used to measure total alkalinity (potentiometric method), total hardness (titrimetric method with Eriochrome black T indicator), and calcium (EDTA titrimetric method with hydroxynaphthyl indicator). Total dissolved solids were measured using a Chemtrix Type 700 conductivity meter. The pH was measured by a Corning Model 7 pH meter. Chloride was measured with the Orion Research Ionanalyzer meter Model 407-A and with the Dionex Autoion System 12 Analyzer Ion Chromatograph. The eluent for the ion chromatograph was a mixture of sodium carbonate and sodium bicarbonate, and the columns were regenerated with sulfuric acid. The chromatograph gave more reliable results and thus was used for most of the samples. Barium was measured using a Perkin Elmer 370 Atomic Absorption unit. The procedure followed that given in Standard Methods (1), except sufficient sodium chloride was added to prevent the ionization of barium.

The sludge and backwash water samples were analyzed for Ra^{226} and Ra^{228} at the Argonne National Laboratory (2). To determine the concentration

of Ra^{226}, they monitored the gamma radiation of Bi^{214} at 609 KeV. Room backgrounds were subtracted, and the calculation was based upon the net count and standard calibrations. Ra^{228} was measured similarly by analyzing Ac^{228} at 911 KeV instead o. Bi^{214} at 609 KeV. National Bureau of Standards standard reference samples were used to calibrate the instruments.

The remaining samples were analyzed by the University of Iowa Hygienic Laboratory. Their procedure determined radium, precipitated with barium sulfate, by alpha counting. Lead and barium carriers were added to the sample containing alkaline citrate, and then sulfuric acid was added to precipitate radium, barium, and lead as sulfates. The precipitate was purified by washing with nitric acid, dissolving in Alkaline EDTA, and reprecipitating as radium-barium sulfate after adjusting the pH to 4.5. Detailed information is given in the University Hygienic Laboratory Radiochemistry Section Standard Operations Procedure Manual (3). EPA reference samples were periodically analyzed to check the accuracy of the procedure.

SECTION 4

RESULTS AND DISCUSSION

A. Radium Removal in Iron and Manganese Removal Plants

Table Grove, IL was the first iron and manganese removal plant sampled. Aeration and chlorination preceed filtration for iron removal. The flow rates and a schematic of the process are presented in Figure 1. The laboratory results for hardness, calcium, total dissolved solids, pH, chloride, alkalinity, and radium are presented in Table 2. Backwash samples were not available.

Adair, IA was another plant that was sampled during the study. Only aeration preceeded the greensand filter, as presented in Figure 2, and the results of the water analyses are presented in Table 3.

The plant located in Stuart, IA has a design similar to the Table Grove, IL plant, but has a detention period directly following aeration (see Figure 3). The water composition is given in Table 4.

Iron and manganese can color waters red and brown-black, respectively. These metals are often treated by aeration and detention followed by filtration to remove the Fe(III) and Mn(IV) precipitates. Radium removal during aeration and detention has been observed (4), perhaps due to adsorption of the radium on the manganese oxides or iron hydroxides. The hydrous oxides of Fe(III) and Mn(IV) have high sorption capacities for bivalent metal ions (5). The greensand filters may remove the manganese as Mn^{2+} and retain it until it is oxidized to Mn(IV). The Mn(IV) is then removed as the MnO_2 precipitate.

The radium removal efficiencies calculated from the data in Tables 2-4 are presented in Table 5, together with previously published data for the same plants and other comparable plants. The removal efficiencies range

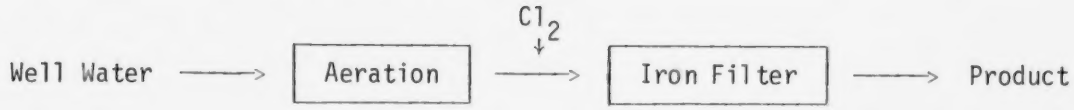

Figure 1. Process schematic for Table Grove, IL.

Figure 2. Process schematic for Adair, IA
(Flow rate: 45,000 gpd).

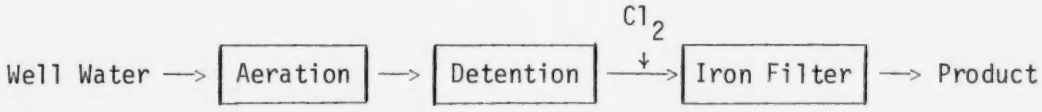

Figure 3. Process schematic for Stuart, IA
(Flow rate: 140,000 gpd).

Table 2

Table Grove, IL, Water Analyses

Location	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ra^{226} (pCi/L)	Ra^{228} (pCi/L)
Raw	250	679	158	3,264	938	7.5	18.4	3.0
After Aeration	244	681	158	3,136	938	7.9	NA	NA
Product Water	237	703	166	3,200	953	7.9	15.7	7.0

Table 3

Adair, IA, Water Analyses

Location	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ra^{226} (pCi/L)	Ra^{228} (pCi/L)
Raw	155	675	224	1,920	378	7.5	10.0	2.9
Product Water (Before Cl_2 added)	151	680	208	1,600	378	7.6	9.1	3.4
Begin Backwash	163	675	180	1,664	NA	7.4		
Middle Backwash	161	670	176	1,760	NA	7.4	21.2*	5.7*
End Backwash	155	668	186	1,760	NA	7.6		

* These values are the average for the total backwash water volume of 1,600 gallons.

Table 4

Stuart, IA, Water Analyses

Location	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ra^{226} (pCi/L)	Ra^{228} (pCi/L)
Raw	179	608	156	1,600	272	7.6	8.9	<0.5
After Aeration & Detention	176	615	156	1,664	322	7.8	NA	NA
Begin Backwash	225	628	144	1,600	NA	7.5	106*	20*
End Backwash	172	603	152	1,600	NA	7.7		
Product Water	165	606	158	1,600	358	7.3	11.2	3.1

* These values are the average for the total backwash water volume of 3,600 gallons.

Table 5

Radium Removal Efficiencies of Iron and Manganese Removal Plants

Location/Date	Ra^{226} Raw (pCi/L)	Ra^{226} Product (pCi/L)	% Removal	Ra^{226} in Backwash Water (μCi)	% of Influent Ra Removed Based on Backwash Concentration	Reference
Adair, IA						
9/18/74	6.6	6.6	4.5	1.2	23.0	6
5/13/75	13.0	8.0	38.0	0.8	27.6	6
8/83	10.0	9.1	9.0	0.1	8.6	This Study
Stuart, IA						
10/22/74	16.0	12.0	25.0	7.6	6.4	6
7/77	11.7	10.0	14.5	NA	NA	7
11/80	9.9	NA				7
8/83	8.9	11.2	-26.0	1.4	4.0	This Study
Table Grove, IL						
8/83	18.4	15.7	15.0	NA	NA	This Study
Eldon, IA						
9/13/74	49.0	43.0	12.0	1.6	9.6	6
8/83	46.7	42.4	9.2	NA	NA	This Study
Estherville, IA						
10/8/74	5.7	5.1	11.0	0.3	9.7	6
Holstein, IA						
10/29/74	13.0	7.2	28.0	0.02	0.5	6
Herscher, IL						
3/25/75	14.9	6.9	54.0	NA	NA	8
4/1/75	14.2	7.0	51.0	NA	NA	8
4/8/75	14.1	6.4	54.0	NA	NA	8

Note: Holstein, Herscher, Estherville, and Eldon have ion exchange following the iron and manganese filter.

from a negative value (possibly due to overloading of the filter) to about 50%, but values in the range of 5% to 15% are most common. The removals based on the quantity of radium in the backwash water are different than those calculated from plant influent and effluent sample analyses, but the differences are reasonable considering that grab samples were used. The recorded removals of 4% or less and 8% to 9% for Stuart and Adair can be compared to previously reported values of 25% and 40%, respectively (6). Since one of the filters at the Adair plant was shut down for repairs, the low efficiency of the plant may be due to the overloading of the one operating filter. From the same EPA report (6), radium removal dropped from 38% to 5.7% during a period of inadequate permanganate addition.

The presence of $MnO_{2(s)}$ on the filters seems to be important for radium removal. Moore and co-workers (9) have reported a high affinity of radium for $MnO_{2(s)}$. The high removals (~50%) given for Herscher, IL in Table 5 were reported to have occurred when about 0.5 mg/L manganese was being removed as $MnO_{2(s)}$ on the filter. Periodic low removals then would be expected after filter backwashing when the $MnO_{2(s)}$ was removed from the filter.

Ra^{226} in the backwash water was found to be 21 pCi/L at Adair and 106 pCi/L at Stuart. These levels are relatively low, and provision of quiescent conditions, in a lagoon for example, should permit the solids to settle out. The supernatant could then be recycled to the plant, but at some time arrangements would have to be made for dealing with solids that accumulate in the lagoon.

B. Radium Removal in Lime Softening Plants

The lime softening plants that were studied were Bushnell, IL, Elgin, IL, Colchester, IL, and West Des Moines, IA. The process schematics for these plants are given in Figures 4-7, and the sampling results are presented in Tables 6-9. The values shown are for grab samples and a more detailed analysis program would be required to obtain long-term averages.

Bushnell discharges its sludge directly into the sanitary sewer. This method of disposal is not a popular means of disposal because the waste-

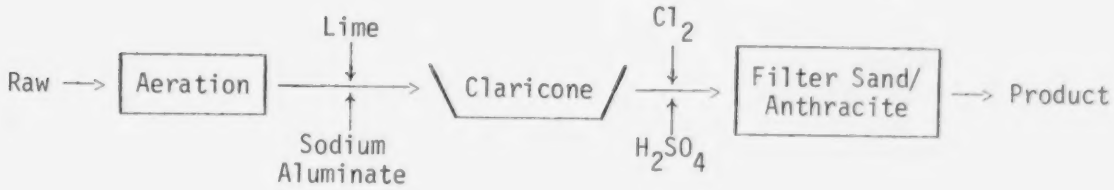

Figure 4. Process schematic for Bushnell, IL (Plant flow rate is 500,000 gpd).

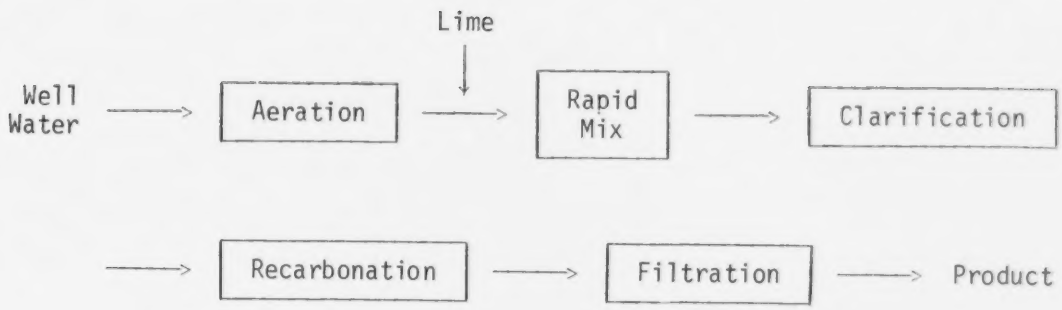

Figure 5. Process schematic for Elgin, IL (Well #5A (only): Flow rate is 2,200,000 gpd; Blended flow rate unknown - assumed 6 MGD).

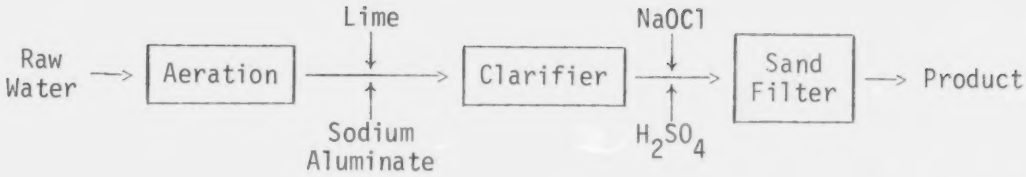

Figure 6. Process schematic for Colchester, IL (Flow rate is 125,000 gpd).

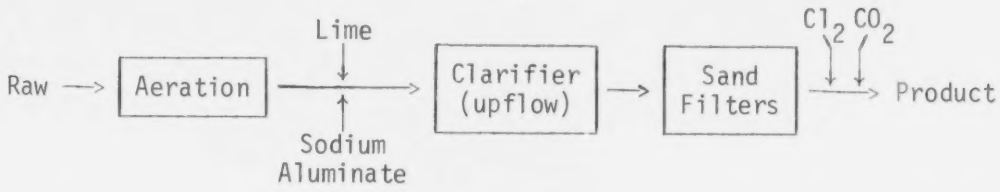

Figure 7. Process schematic for West Des Moines, IA (Flow rate is 2 MGD).

Table 6

West Des Moines, IA, Water Analyses

Location	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca^{2+} (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ra^{226} (pCi/L)	Ra^{228} (pCi/L)
Raw Water	283	389	100	1,120	55	7.4	6.9	0.5
After Aeration	286	392	136	1,120	55	7.6	NA	NA
Clarifier Effluent	70	135	50	960	55	10.0	NA	NA
After Cl_2 & CO_2	71	142	38	928	66	9.6	NA	NA
After Filtration	76	152	36	960	57	9.5	1.5	0.5

	Ra^{226}		Ra^{228}	
	pCi/L	pCi/g(dry)	pCi/L	pCi/g(dry)
Clarifier Sludge*	<19	<1.2	<39	<2.4
Lagoon Sludge*	5,160	10.8	600	1.2
Backwash Water*	NA	NA	NA	NA

*Based on grab samples

Table 7

Bushnell, IL, Water Analyses

Location	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca^{2+} (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ra^{226} (pCi/L)	Ra^{228} (pCi/L)
Well Water	192	354	85.2	1,792	390	7.8	12.6	<0.5
Before Claricone	210	392	93.3	1,600	390	7.8	NA	NA
After Claricone	51.3	214.5	63.3	1,856	322	8.4	NA	NA
After Cl_2	22.4	216.5	65.7	1,760	337	9.7	NA	NA
After Filter	30.8	207	63.3	1,856	352	10.0	6.9	0.6

	Ra^{226}		Ra^{228}	
	pCi/L	pCi/g(dry)	pCi/L	pCi/g(dry)
Sludge	4,577	21.6	<45	<0.2

Table 8

Elgin, IL, Water Analyses

Location	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ba^{2+} (mg/L)	Ra^{226} (pCi/L)	Ra^{228} (pCi/L)
Raw Water	315	253	67	208	NA	6.8	4.0	0.3*	<0.9
After Aeration	311	244	73	448	4.5	7.3	6.8	NA	NA
Rapid Mix	297	247	63.5	416	5	7.9	NA	NA	NA
Clarifier #1 Effluent	103	75	11	211	15	9.3	NA	0.9	<0.9
Clarifier #2 Effluent	133	95.5	19	240	14	9.2	0.4	NA	NA
Before Recarbonation	106	82	21	288	16	9.5	NA	NA	NA
After Recarbonation	102	83.5	13	237	17	9.4	0.7	NA	NA
Filter Influent	96.5	75	7	211	21	8.9	0.5	NA	NA
Filter Effluent	81	83	9	166	28	8.9	0.4	NA	NA
Finished Water	101	84	10	160	23	9.2	NA	0.5	3.5

	Ra^{226}		Ra^{228}	
	pCi/g(dry)	pCi/L	pCi/g(dry)	pCi/L
Lagoon (active) Sludge	11.3	9,642	11.7	9,939
Lagoon (inactive) Sludge	10.9	11,686	11.3	12,167
Clarifier Sludge	8.6	948	8.0	873
Backwash Water	<0.02	<20	<0.04	<40

*Values determined by Gilkeson (13) in May, 1983 were 7.1 to 8.8 pCi/L.

NOTE: All values, except raw water values, are averages of samples from two wells.

Table 9

Colchester, IL, Water Analyses

Location	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca^{2+} (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ra^{226} (pCi/L)	Ra^{228} (pCi/L)
Raw Deep Well	231	698	170	2,880	773	7.5	24.2	1.0
Raw Shallow Well	272	324	85	512	20	7.1	NA	NA
After Aeration	252	504	130	1,760	373	7.3	NA	NA
Clarifier Effluent	43	281	51	1,600	307 (est.)	9.6	NA	NA
Filter Influent	22	297	57	1,664	383	7.8	NA	NA
Finished	23	298	55	1,600	383	8.3	3.1	0.7

	Ra^{226}		Ra^{228}	
	pCi/L	pCi/g(dry)	pCi/L	pCi/g(dry)
Backwash Water	<19.5		<39	
Clarifier Sludge	2,038	15	236	1.7

Table 10

Radium and Hardness Removal Efficiencies in Lime Softening Plants

Location/Date	Ra^{226} (raw water) pCi/L	Ra^{226} % Removed	Total Hardness (raw water) mg/L as $CaCO_3$	Total Hardness % Removed	Reference
W. Des Moines, IA					
8/1/74	9.3	75	376	49	11
6/5/78	1.9	43	NA	NA	20
8/2/83	6.9	78	389	61	This Study
Webster City, IA					
8/13/74	6.1	85	507	48	11
2/20/75	7.8	96	482	78	11
7/26/78	1.4	60	NA	NA	20
Peru, IL					
2/20/75	6.5	92	329	47	11
2/25/75	5.5	70	278	35	11
3/4/75	5.5	76	286	57	11
Elgin, IL					
3/7/75	7.5	90	246	60	11
3/14/75	5.7	86	243	54	11
3/21/75	3.5	80	242	61	11
6/27/83	0.3	(-)	253	67	This Study
Colchester, IL					
8/83	12.1	74	698	57	This Study
Bushnell, IL					
8/83	12.6	45	354	42	This Study

water treatment plant operator must agree to accept the material at variable rates and concentrations, and such agreements are difficult to obtain (10). Often, this method is used when both the water plant and wastewater plant are owned or operated by the same organization and co-treatment may reduce costs. While this procedure is acceptable for some plants, it may simply result in a transfer of the problem from the water treatment plant to the wastewater treatment plant. Singley (11) notes that sludge discharged from the wastewater plant would have the same amount of radium as the sludge from the water plant.

At Elgin the clarifier sludge is pumped to nearby temporary drying lagoons. These lagoons are used to concentrate the sludge discharges. Two lagoons are used intermittently; thus one lagoon (active) can provide storage for current sludge discharges while the other (inactive) serves to dry the sludge before removal. When the sludge is concentrated so that it can be easily handled, it is hauled to permanent lagoons for ultimate disposal. Lagooning of softening sludges is very popular because more than 50% dewatering is possible. Also, permanent lagoons can be reclaimed for use as parking lots, golf courses, playgrounds and parks. Lagoons can also be good foundations for sanitary landfills. Home building on these reclaimed lagoon sites is discouraged, however, when radium contaminated sludge is present, due to the production of radon gas which is hazardous to the lungs (12). Colchester disposes of its waste in lagoons similar to Elgin's, although temporary lagooning is not used.

The current practice at West Des Moines is to dispose of sludge in a drying lagoon. In the past, this lagoon was cleaned out periodically and the sludge was hauled to either a landfill or utilized in a concrete plant. Recent changes, however, have rendered these options infeasible. Operators at this treatment plant are currently investigating possible ultimate disposal site alternatives.

Radium removal at the plants sampled this summer ranged from 45% at Bushnell to 78% at West Des Moines (see Table 10). The value from the Bushnell plant is uncharacteristically low; the Elgin results were very low because water which did not contain radium was blended with the well

water containing radium. The other values approach 70% removal efficiency. Others report radium removal efficiencies between 70% and 92% (6,8). Bennett et al. found the removal efficiency at Elgin and Peru to be 86% to 88.9% and 70.6% to 92.4%, respectively, for samples taken over a three week period (8). Lime-soda ash plants investigated by Singley et al. (11) removed 59% to 96% of the radium, and averaged 80% removal. There is some indication that the pH of treatment may be an important factor that determines the extent of removal (5), but this remains a topic for additional study. Further, the role of $Mg(OH)_{2(s)}$ precipitate in affecting the extent of removal should be determined.

The relationship between hardness and radium has also been examined. Singley et al. (11) compared Ra^{226} removal with the total hardness removal and found the following correlation:

$$y = x^{2.86}$$

where y = total hardness removal fraction, and x = Ra^{226} removal fraction. This correlation is shown in Figure 8, together with the data from Table 10. A similar empirical correlation which gives a better fit of the data is

$$y = 0.4566 \frac{y}{x} + 0.2275$$

as shown in Figure 9 (Curve 1). The fit of the data can be further improved if the Bushnell and Florida points are ignored (Curve 2), in which case the equation is

$$y = 0.8911 \frac{y}{x} + 0.0376$$

Brinck et al. (5) also collected and analyzed the sludge and filter backwash water from lime softening plants. Our data, in addition to theirs, are presented in Table 11. The sludge concentrations of Ra^{226} range from 1,000 to 11,000 pCi/L of sludge, with the concentration depending upon the percent solids in the sludge. The concentration per dry gram of solids is

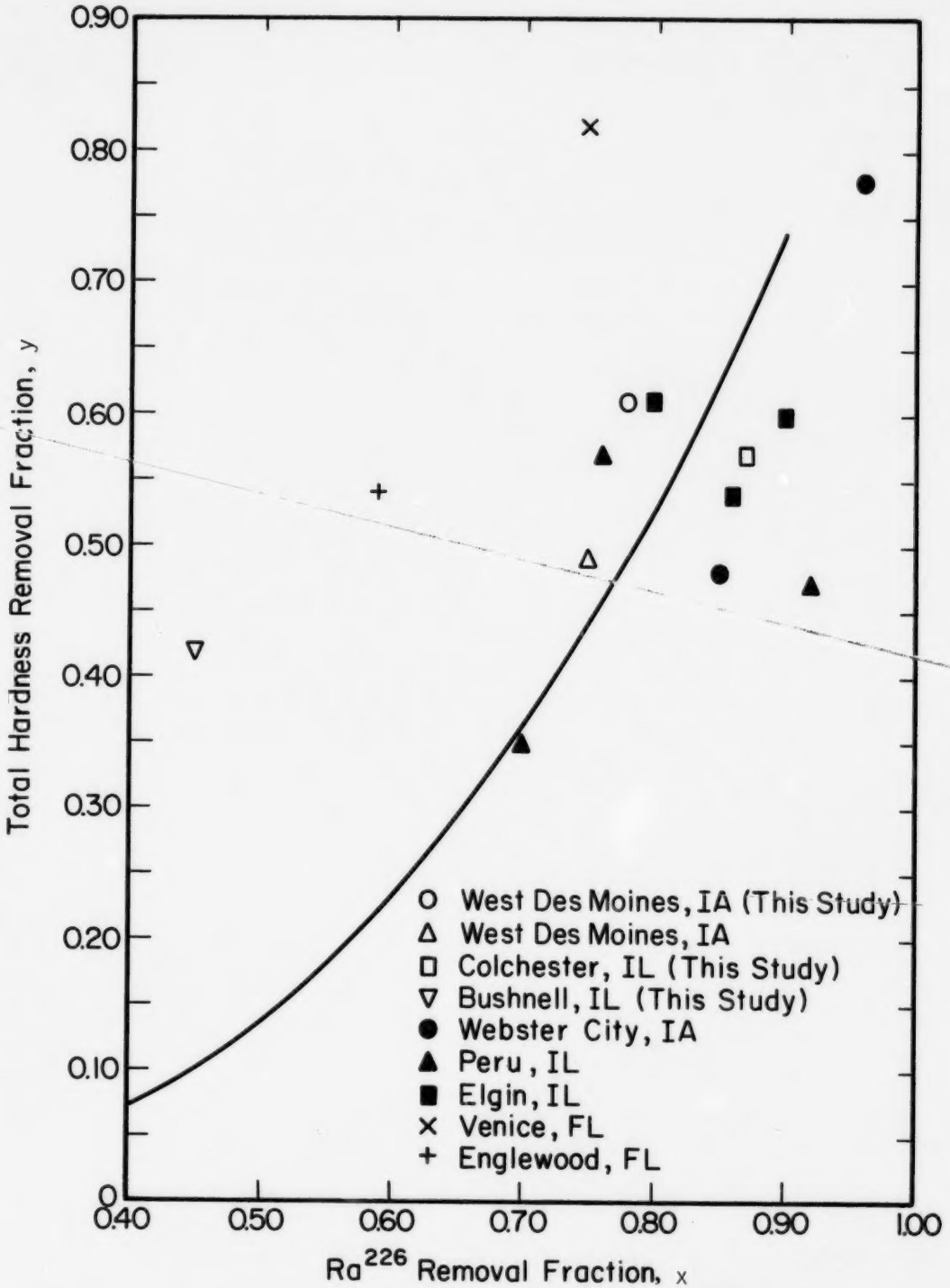

Figure 8. Comparison between total hardness and Ra^{226} removal fractions for lime softening plants.

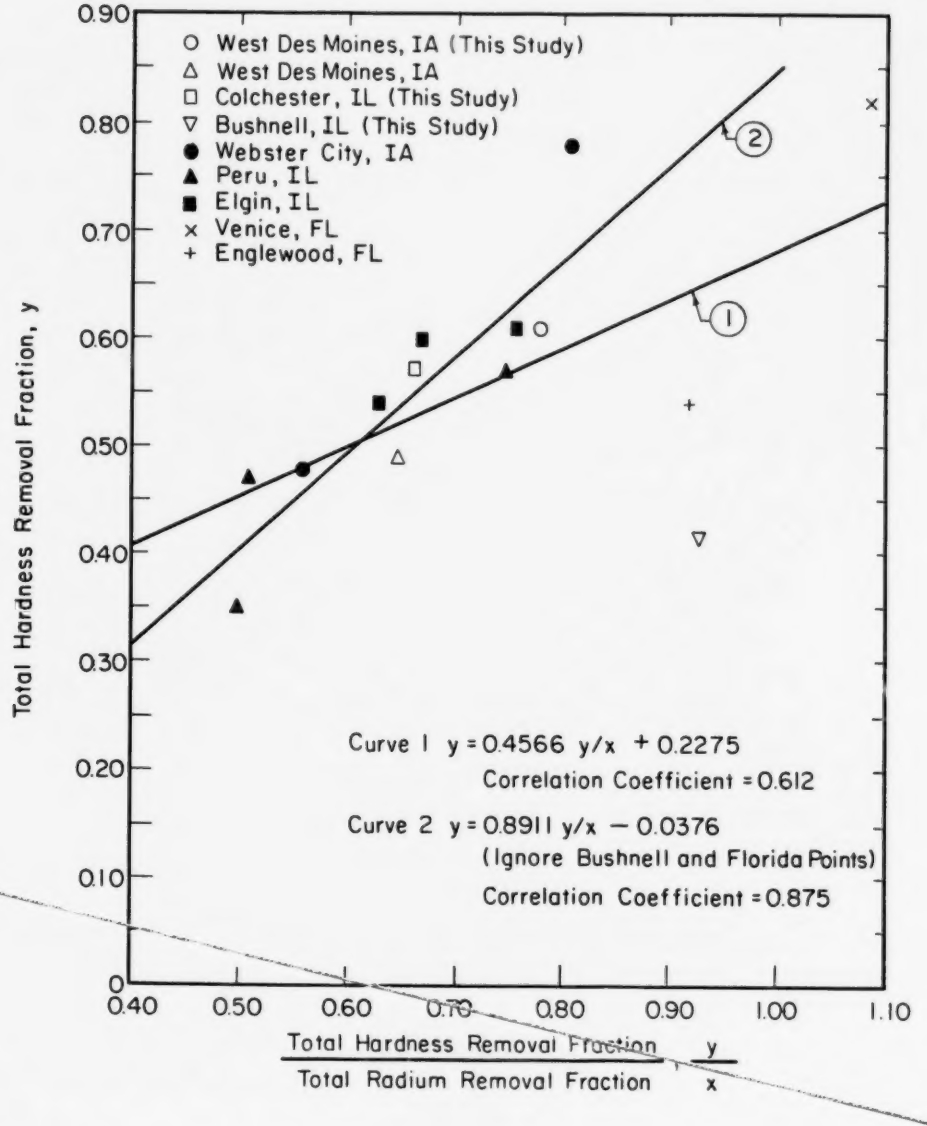

Figure 9. Proposed correlation between Ra^{226} and total hardness removal fractions for lime softening plants.

Table 11

Summary of Radium Concentrations in Lime Softening Sludges and Backwash Waters

Location	% Solids	Ra^{226} (pCi/L)	Ra^{228} (pCi/L)	Ra^{226} pCi/g(dry)	Ra^{228} pCi/g(dry)	Reference
W. Des Moines, IA						
Lagoon Sludge	37.6	5,159	596	10.8	1.3	This Study
Clarifier Sludge*	1.6	<20	<40	<1.2	<2.4	This Study
Lagoon Sludge	NA	2,300	NA	NA	NA	5
Backwash Water	NA	6.3	NA	NA	NA	5
Bushnell, IL						
Clarifier Sludge	19	4,577	<45	21.6	<.21	This Study
Colchester, IL						
Clarifier Sludge	12.6	2,038	236	15.0	1.7	This Study
Backwash Water	0.23	<20	<39	NA	NA	This Study
Webster City, IA						
Sludge	NA	980	NA	NA	NA	5
Backwash Water	NA	50	NA	NA	NA	5
Peru, IL						
Backwash Water	NA	36.9	NA	NA	NA	5
Elgin, IL						
Active Lagoon Sludge	57.3	9,642	9,939	11.3	11.7	This Study
Inactive Lagoon Sludge	67.1	11,686	12,167	10.9	11.3	This Study
Clarifier Sludge	10.3	948	873	8.6	8.0	This Study
Backwash Water	0.051	<20	<40	<.02	<.04	This Study
Sludge	NA	6,100	NA	NA	NA	5
Backwash Water	NA	18.3	NA	NA	NA	5

*Assume specific gravity = 1.0.

10 to 20 pCi/gram. Backwash water concentrations of Ra^{226} range from 6 to 50 pCi/L, and most of this radium is probably in the form of solids.

The quality of the data on radium concentration in sludge was checked by determining the concentration that should be present (theoretical) based on the differences between influent and effluent radium and hardness concentrations. The theoretical and actual concentrations (see Table 12) could then be compared. The measured values range from 88% smaller to 37% larger than the calculated values; possible reasons for the differences include uncertainties in the calculation of the quantity of sludge produced, the difficulty of obtaining data that represent long-term operation results from grab samples, and the possibility that the analytical procedure may not recover all the radium from the sludge.

The theoretical volumes of sludge produced at the four softening plants, West Des Moines, Colchester, Bushnell, and Elgin were calculated according to the procedure published by the AWWA Committee on Lime Softening (10). The method involves the use of the equation,

$$S = 86.4\ Q\ (2.0\ Ca + 2.6\ Mg + 1.9\ Fe + SS + A)$$

where

Q = plant flow (m^3/sec)
Ca = calcium hardness removed (mg/L as $CaCO_3$)
Mg = magnesium hardness removed (mg/L as $CaCO_3$)
Fe = iron dose (mg/L as Fe)
SS = raw water suspended solids (mg/L)
A = additional chemicals, carbon, potassium permanganate (mg/L)
S = sludge production (dry weight) in kg/day

The concentration of Fe and SS removed was assumed to be zero and it was assumed that no additional chemicals were added. Further, it was assumed that 97% of the radium that was removed will appear in the sludge (11).

C. Radium Removal in Ion Exchange Softening Plants

Samples from the water treatment plant at Eldon, IA were analyzed to yield information on the ability of ion exchange units to remove radium from groundwaters, and on the concentration of radium in the process

Table 12

Theoretical Sludge Quantities and Theoretical and Measured Ra^{226} Concentrations

Plant	Theoretical Sludge Production (Kg solids/day)	Theoretical Ra^{226} Concentration (pCi/g(dry))	Measured Ra^{226} Concentration* (pCi/g(dry))	% Diff.
W. Des Moines	3,955	10.0	<1.2**	-88
Colchester	323	24.0	15	-37.5
Bushnell	712	15.8	21.6	+36.7
Elgin	8,090	(-)	0.9	NA

*Based on concentrations measured in the clarifier sludge.

**Lagoon sludge contained 10.8 pCi/g dry Ra^{226}, a +8% difference.

wastewater. A schematic diagram of the treatment plant is given in Figure 10. The fraction of raw water which by-passed the ion exchange columns was not determined because flow meters were absent.

Chemical analyses of the water at different points in the treatment process are given in Table 13. A chemical analysis of the wastewaters produced from regeneration with a 40%- and 100%-saturated solutions of sodium chloride are given in Table 14. Both columns are usually regenerated with a 100%-saturated solution (26% to 37% by weight), but a shortage of available salt resulted in the decision to regenerate one column with a 40%-saturated solution (10% to 15% by weight). Although complete regeneration with a 40%-saturated brine is possible, an insufficient quantity of it was applied. Eldon's spent brine is discharged to a storm sewer which flows to a river.

The Ra^{226} removal obtained by ion exchange at Eldon was 60%, assuming an average effluent concentration of 17.2 pCi/L. However, it should be remembered that this regeneration was performed with a limited amount of 40%-saturated salt solution and that the regeneration was incomplete. This removal compares with the 65% to 85% removals found by Singley et al. (11) for plants which were incompletely regenerating their exchange media. Singley et al. notes that 95% removal, or better, of radium can be expected in a well-operated ion exchange plant (11). His survey of eight ion exchange plants (4 in Iowa, 3 in Illinois, 1 in Florida) indicated radium removals of 84% to 97%, with raw water Ra^{226} concentrations ranging from 3.3-49 pCi/L. For comparison, Brinck et al. found radium removals of 81% to 97% at seven ion exchange treatment plants in Iowa and Illinois (5). Raw water radium concentrations varied from 3.3-43 pCi/L Ra^{226} in these plants. Schliekelman et al. performed an extensive study of Iowa water treatment plants and found ion exchange plants to remove 93% to 96% of Ra^{226} from raw waters containing 5.7-49 pCi/L (6).

Other studies have been done to determine the applicability of ion exchange softening plants for radium removal. Snoeyink et al. performed lab studies on both strong and weak acid resins (17). It was found that good radium removal occurred long after hardness breakthrough for both

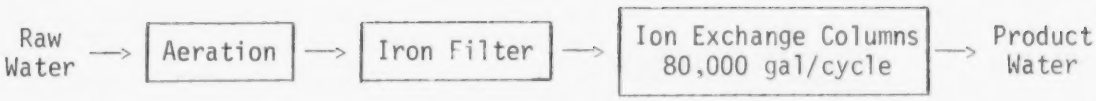

Figure 10. Process schematic for Eldon, IA. The columns were regenerated after 60,000 and 70,000 gallons. The total flow rate is 360,000 gpd.

Table 13

Eldon, IA, Water Analyses

Location	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca^{2+} (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ra^{226} (pCi/L)	Ra^{228} (pCi/L)
Raw	248	340	88	1,280	185	7.5	46.7	2.8
After Aeration	247	345	89	1,280	234	7.6	NA	NA
After Fe Filter	248	349	104	1,254	191	7.7	42.4	1.6
Product Just After Regen. (Column 1)	235	175	44	1,344	240	7.8	14.2	<0.9
Product 1 Hr After Regen. (Column 1)	242	155	37	1,280	248	7.9	NA	NA
Product After 60,000 Gal (Column 1)	232	304	92	1,280	167	7.8	20.1	1.1
Product After 58,000 Gal (Column 2)	229	270	65	1,280	182	7.5	NA	NA

Note: Backwash water volume: 1,750 Gal
Brine volume: 50 Gal
Rinse water volume: 5,250 Gal

Table 14

Eldon, IA, Wastewater Analyses
40% Saturated Sodium Chloride (Column 1)

	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca^{2+} (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ra^{226} (pCi/L)	Ra^{228} (pCi/L)
Backwash	248	335	86	1,280	136	7.8	39	1.9
Start Regeneration	243	340	96	1,280	192	7.7	33 (ave.)	1.3 (ave.)
Regeneration 6 Min	223	390	114	1,344	268	7.4		
Regeneration 13 Min	178	2,500	550	4,800	3,100	7.2	110	<40
Begin Rinse	167	3,020	760	5,570	3,020	7.2	210 (ave.)	12 (ave.)
Rinse 5 Min	202	3,391	790	6,336	4,800	7.2		
Rinse 10 Min	204	3,691	840	6,900	4,380	7.3	217	<40
Rinse 20 Min	207	3,616	890	7,200	4,680	7.2	39.9* (ave.)	0.5* (ave.)
Rinse 30 Min	283	1,280	310	3,520	1,740	7.7		
Rinse 50 Min	251	349	108	1,760	468	7.7	NA	NA
Rinse 70 Min	246	239	57	1,440	162	7.7	39.9* (ave.)	0.5* (ave.)
Rinse 90 Min	239	205	48	1,440	380	7.4		
Rinse 120 Min	238	189	49	1,400	436	7.6	NA	NA

* This average is for all four samples.

Table 14 (Continued)

100% Saturated Sodium Chloride (Column 2)

	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca^{2+} (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ra^{226} (pCi/L)	Ra^{228} (pCi/L)
Backwash	238	359	88	1,280	NA	7.6	NA	NA
Start Regeneration	240	347	87	1,280	191	7.7	NA	NA
Regeneration 5 Min	238	330	78	1,280	202	7.7	NA	NA
Regeneration 10 Min	168	8,229	1,899	10,240	8,500	7.1	NA	NA
Rinse 10 Min	180	17,706	5,197	35,840	22,600	7.0	1,144	<40
Rinse 20 Min	191	14,962	3,898	39,700	24,900	7.0	NA	NA

types of resin, although operation through several production cycles with incomplete regeneration may have led to poorer removals. When sufficient regenerant was applied, some Ra^{226} accumulated on the strong acid resin only for a few cycles after new resin was put into use. This accumulation did not lead to poor removal. The weak acid resin showed very little accumulation of Ra^{226}.

A comparison of hardness and radium removal is presented in Table 15. These data indicate a direct correlation between the amount of hardness and radium removed. Therefore, even though radium removal occurs after a significant hardness breakthrough, an extended service cycle may cause Ra^{226} concentrations to exceed the MCL when treating raw water high in radium(17).

Ra^{226} concentrations in the spent brine from the column regenerated with the 40%-saturated sodium chloride (10% to 15% by weight) were determined from composites of grab samples. The concentration profile through the regeneration cycle is shown in Figure 11. Only 33% of the Ra^{226} placed on the column was removed in the wastewater, consistent with incomplete regeneration because an insufficient amount of salt was applied. Of this 33%, 4.5% was removed during backwashing, 2.3% was removed during brine application, and 26.5% was removed in the rinse cycle. The average Ra^{226} concentrations in the backwash, brine, and rinse wastewaters are 39 pCi/L, 68 pCi/L, and 76.5 pCi/L, respectively. Eldon produces 9.4 gallons of wastewater (backwash included) per 100 gallons of water softened.

The second ion exchange column at Eldon which was regenerated with a 100%-saturated sodium chloride solution, produced a wastewater that had a much higher concentration of TDS and other constituents (see Table 14). Only one grab sample was analyzed for Ra^{226}, but it can be seen that the concentration of Ra^{226} after 10 minutes of rinse is much higher (1,144 pCi/L compared to 217 pCi/L) in the wastewater produced from the 100%-saturated sodium chloride solution than that from the 40%-saturated solution. This indicates the importance of proper plant operation in the removal of radium.

Table 15

Hardness and Ra^{226} Removals in Ion Exchange Plants

Location	Ra^{226} In (pCi/L)	Ra^{226} Out (pCi/L)	Ra^{226} (% Removed)	Total Hardness in Raw Water (mg/L as $CaCO_3$)	Total Hardness in Product Water (mg/L as $CaCO_3$)	Total Hardness Removed (%)	Reference
Hersher, IL							
3/25/75							8
Just After Regeneration	6.6	1.3	81.2	412	18	95.6	
Midpoint	6.9	0.4	93.9	427	12	97.2	
Near Breakthrough	6.9	2.1	69.9	417	184	55.8	
Dwight Correctional Center, IL							
2/13/75-2/14/75							8
Just After Regeneration	3.	0.4	88.0	286	16.0	94.3	
Midpoint	3.3	0.3	92.5	284	4.1	98.6	
Near Breakthrough	3.	1.0	70.7	279	131.0	53.7	
Eldon, IA							
8/83							This Study
Just After Regeneration*	NA	14.2	66.5	NA	175	50	
Midpoint	42.4	NA	NA	350	NA	NA	
Near Breakthrough	NA	20.1	52.6	NA	232	33.7	

*40% saturated brine

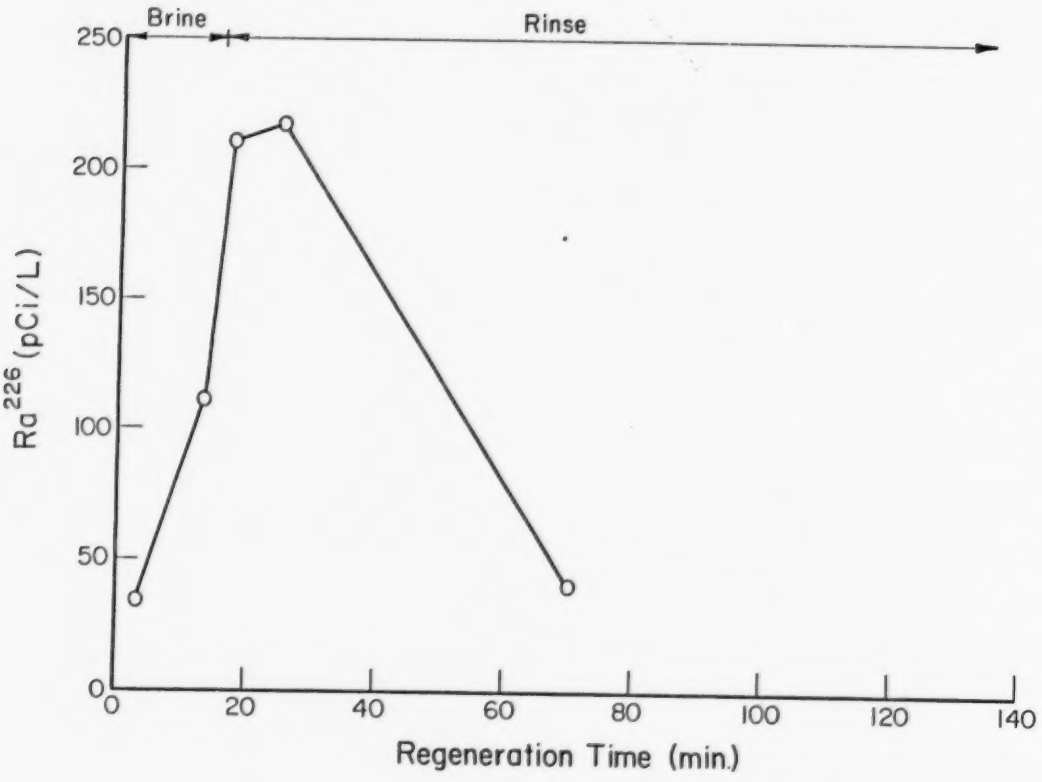

Figure 11. Variation of Ra^{226} concentrations during regeneration at Eldon, IA (10-15% NaCl brine).

A study of seven water treatment plants reported maximum Ra^{226} concentrations in softener brine and rinse effluent to range from 320-3,500 pCi/L (5). Iowa ion exchange wastes were found to contain 7.8-94 pCi/L of Ra^{226} in the backwash water, and rinse wastewaters ranged from 114-1,960 pCi/L of Ra^{226} (6). Wastewater volumes generated were 2% to 10% of the product water in the above study.

Ranges of average chemical constituents for regeneration wastewaters are presented in Table 16. Table 17 shows average Ra^{226} concentrations at four ion exchange plants in Iowa. From these data, one can see that the wastewater characteristics vary greatly from one plant to another.

D. Barium Removal in Lime Softening Plants

Barium removal at Elgin was found to be 90% at a pH of 9.3 (see Table 8). Sorg and Logsdon found that barium removal is pH dependent (Table 18), with an optimum pH between 9 and 11 (18). Above pH 11, soluble barium hydroxide may form and decrease removal efficiencies (18).

E. Barium Removal in Ion Exchange Treatment Plants

Crystal Lake, IL treats groundwater containing barium by an ion exchange process. The system is composed of three separate wells, with two strong-acid ion exchange columns for each well. Water and spent brines were analyzed at two of these ion exchange wells (Well #6 and Well #8). The plant characteristics are shown in Table 19. Chemical analyses of the water during the service and regeneration cycles are presented in Tables 20 and 21, respectively. Crystal Lake discharges its spent brine into a sanitary sewer system, which eventually discharges to the wastewater treatment plant.

Both ion exchange plants in Crystal Lake removed 92% of the incoming barium after start-up of the service cycle. Removal at Well #8 dropped to 54%, however, just before regeneration. Sorg and Logsdon also surveyed two full-scale ion exchange softening plants treating groundwater containing barium (18). They found that the plants removed 94% of the incoming barium from raw water containing 10-19 mg/L barium. Laboratory studies by Snoeyink et al. showed that hardness and barium will break through at about the same time for a strong acid resin after

Table 16

Average Chemical Constituents of Ion Exchange Wastewater

Constituents (mg/L)	AWWA Report (1969) (19) Range of Averages	AWWA Report (1969) (19) One Plant's Data	Schiekelman (6) Range of Averages
TDS	15,000 - 35,000	15,656	54,000 - 130,000
Ca^{2+}	3,000 - 6,000	1,720	NA
Mg^{2+}	1,000 - 2,000	600	NA
Hardness (as $CaCO_3$)	NA	7,762	16,000 - 39,000
Na^{+}	2,000 - 5,000	3,325	NA
Cl^{-}	9,000 - 22,000	9,600	9,500 - 120,000

Table 17

Ra^{226} Concentrations in Ion Exchange Treatment Plant Wastewater

Location	Average Brine + Rinse (pCi/L)	Average Brine + Rinse + Backwash (pCi/L)	Average for Peak 1/4 - 1/3 of Regeneration Cycle (pCi/L)	Peak Concentration in Wastewater (pCi/L)	Raw Water Concentration (pCi/L)
Eldon, IA	530	420	2,000	3,500	46
Estherville, IA	NA	52	114	320	5
Grinnell, IA	110	NA	260	320	6
Holstein, IA	175	NA	576	1,100	13

Data from Schliekelman (6).

Table 18

Barium Removals as a Function of pH

Barium Removed (%)	pH
65	8.7
98	10.5
55	11.6

Table 19

Crystal Lake, IL, Water Treatment Plant Data

	Well #6	Well #8
Ion Exchange Units	2	3
Diameter	108"	120"
Height	72"	-
Volume of Resin	164 ft^3	250 ft^3
Resin Height	30"	38"
Free Board	23"	-
Capacity	20 Kgrains/ft^3 (0.9 eq/L)	19 Kgrains/ft^3 (0.87 eq/L)
Water Treated/Cycle	200,000 Gal	350,000 Gal

Regeneration

	Well #6		Well #8	
	Flow Rate (gpm)	Time (min)	Flow Rate (gpm)	Time (min)
Backwash	318	16	400	10
Brine	30 35	12 24 } Total Time is 24 Min	27.25 37	{ 20
Rinse	118	27	slow 37 fast 400	20 10

Table 20

Crystal Lake, IL, Water Analyses
During the Service Cycle

a. Well #6

Sample	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca^{2+} (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ba^{2+} (mg/L)
Raw (average)	245	233	51	324	1	8.0	9.5
Product Just After Regen.	259	33.5	7.3	704	104	8.1	1.1
Product 10 Min After Regen.	253	20	2.8	410	14	8.1	0.6
Product After 45,000 Gal Treated	243	14	1.6	333	1.5	8.1	0.6
Product After 100,000 Gal Treated	243	22	2.4	326	2	8.1	0.1

Table 20 (cont.)

b. Well #8

Sample	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca^{2+} (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ba^{2+} (mg/L)
Raw After Regen.	270	244	70.8	352	3	7.6	16.1
Product Just After Regen.	276	46.4	15.5	768	>100	7.7	none
Product 9 Min After Regen.	276	12.1	3.3	563	27	7.7	0.2
Product After 75,000 Gal Treated	262.5	10.1	2.4	368	1.8	7.5	0.1
Product After 300,000 Gal Treated	269.2	198.8	36.6	371	2.5	7.7	7.4

Table 21

Crystal Lake, IL, Regeneration Wastewater Analyses

a. Well #6

Sample	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca^{2+} (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ba^{2+} (mg/L)
Backwash Begin	247	232	50	326	1.3	8.1	8.1
Backwash End (15 Min)	244	229	47	326	1.3	8.1	5.4
Brine Start	247	229	52	326	3	8.1	9.5
Brine (5 Min)	232	827	166	1,248	411	7.9	22.5
Brine (10 Min)	197	8,576	1,621	9,152	5,780	7.6	243
Brine (15 Min)	170	18,364	3,624	30,400	13,140	7.4	614
Brine (20 Min)	168	25,830	5,375	50,560	NA	7.1	942
Brine End (25 Min) Start Rinse	158	32,700	7,330	102,400	NA	7.0	1,197
Rinse (1 Min)	180	30,320	6,841	67,840	NA	7.1	1,172
Rinse (6 Min)	218	8,828	2,036	32,640	11,790	7.5	221
Rinse (11 Min)	251	2,673	537	7,552	4,690	7.8	54.8
Rinse (16 Min)	267	360	79	2,368	1,058	7.9	1.4
Rinse (26 Min)	263	52	10	890	183	8.1	0.5
Rinse End (27 Min)	265	50	11	832	153	8.1	0.5

Table 21 (cont.)

b. Well #8

Location	Total Alkalinity (mg/L as $CaCO_3$)	Total Hardness (mg/L as $CaCO_3$)	Ca^{2+} (mg/L Ca)	TDS (mg/L)	Cl^- (mg/L)	pH	Ba^{2+} (mg/L)
Backwash Start	264	253	3	368	4.1	7.5	22.1
Backwash (7 Min)	268	234	50	371	2	8.0	16.5
Backwash End (14 Min) Brine Start	267	238	54	371	9.5	7.9	12.3
Brine (2 Min)	266	228	46	333	NA	7.8	9.8
Brine (7 Min)	266	222	42	333	NA	7.9	7.3
Brine (12 Min)	237	3,532	676	3,840	2,478	7.7	112
Brine End (17 Min) Slow Rinse Begin	180	20,231	4,140	11,520	13,290	7.4	724
Slow Rinse (5 Min)	152	32,995	7,262	62,400	NA	7.2	1,464
Slow Rinse (10 Min)	145	44,018	9,976	80,000	15,090	7.1	2,077
Rapid Rinse (17 Min)	162	38,456	10,140	220,000	69,800	6.9	5,162
Rapid Rinse (23 Min)	280	646	131	2,624	1,074	8.0	4.0
Rapid Rinse (27 Min)	280	125	28	1,222	362	8.2	1.5

operation through several exhaustion-regeneration cycles (17). Because the sample showing low barium removal also shows a low hardness removal, the data from Crystal Lake are consistent with the conclusion that barium can be removed to less than the MCL of 1 mg/L if the resin is not saturated with hardness.

At Well #8, 153% of the barium removed by the ion exchange column during the service cycle was found in the regenerant wastewater. The distribution of this barium was 1.8% in the backwash water, 3% in the brine, and 148% in the rinse water. The 10,000 gallons of wastewater produced from one regeneration cycle contained 30 Kg of barium. Every 100 gallons of product water produced 1.7 gallons of wastewater excluding backwash water, and 2.9 gallons/100 gallons including backwash water. More than 100% barium removal during regeneration is possible if the previous regeneration was incomplete.

At Well #6, 84% of the barium placed on the column was removed during regeneration. Almost 2% was removed during backwash, 45% during the brine application, and 37% during the rinse cycle. Six and one-half Kg of barium were contained in the 9,500 gallons of wastewater generated from one regeneration cycle. Every 100 gallons of product water produced 2.2 gallons of wastewater. This value is increased to 4.7 gallons of wastewater/100 gallons of product water when backwash water is included.

Sorg and Logsdon found that the regeneration of the ion exchange plant in their study removed 85% of the barium placed on the column (18). Eighteen Kg of barium was contained in the 9,250 gallons of wastewater generated. The average wastewater barium concentration was 534 mg/L, with a peak concentration of 6,000 mg/L Ba. The wastewater volume generated was 2.6% of the product water.

Barium concentrations in the water and wastewater at Crystal Lake are given in Table 22. Figures 12 and 13 show hardness and barium concentration during regeneration for Wells #6 and #8. By comparing these figures one can see that the peak hardness and barium concentrations coincide at Well #6, but the peak hardness value occurs before the peak barium concentration at Well #8. This phenomenon may be caused by the

Table 22

Crystal Lake's Water and Wastewater Barium Concentrations

	Ba in Raw Water (mg/L)	Peak Ba During Regeneration (mg/L)	Average Concentration in Brine and Rinse Water (mg/L)	Average Concentration in Backwash, Brine and Rinse Water (mg/L)
Well #6	9.5	1,197	328	153
Well #8	16.1	5,161	1,297	789

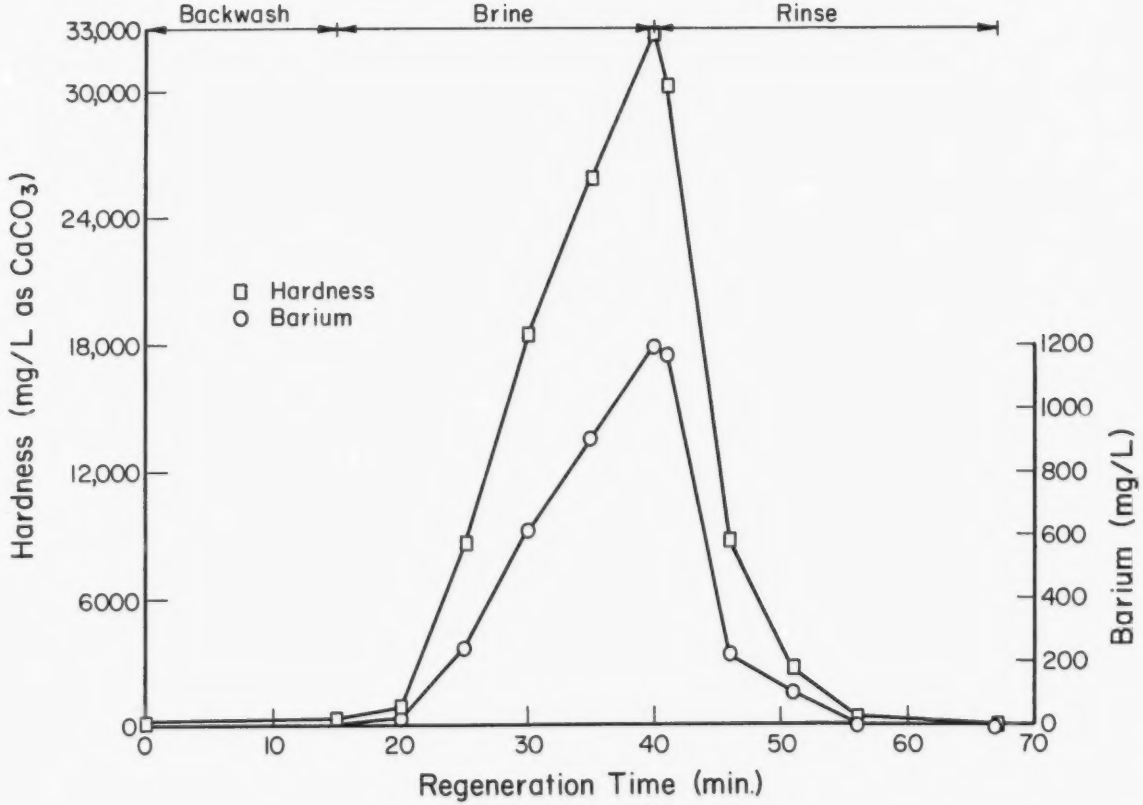

Figure 12. Barium and hardness concentrations in spent brine at Crystal Lake, IL, Well #6.

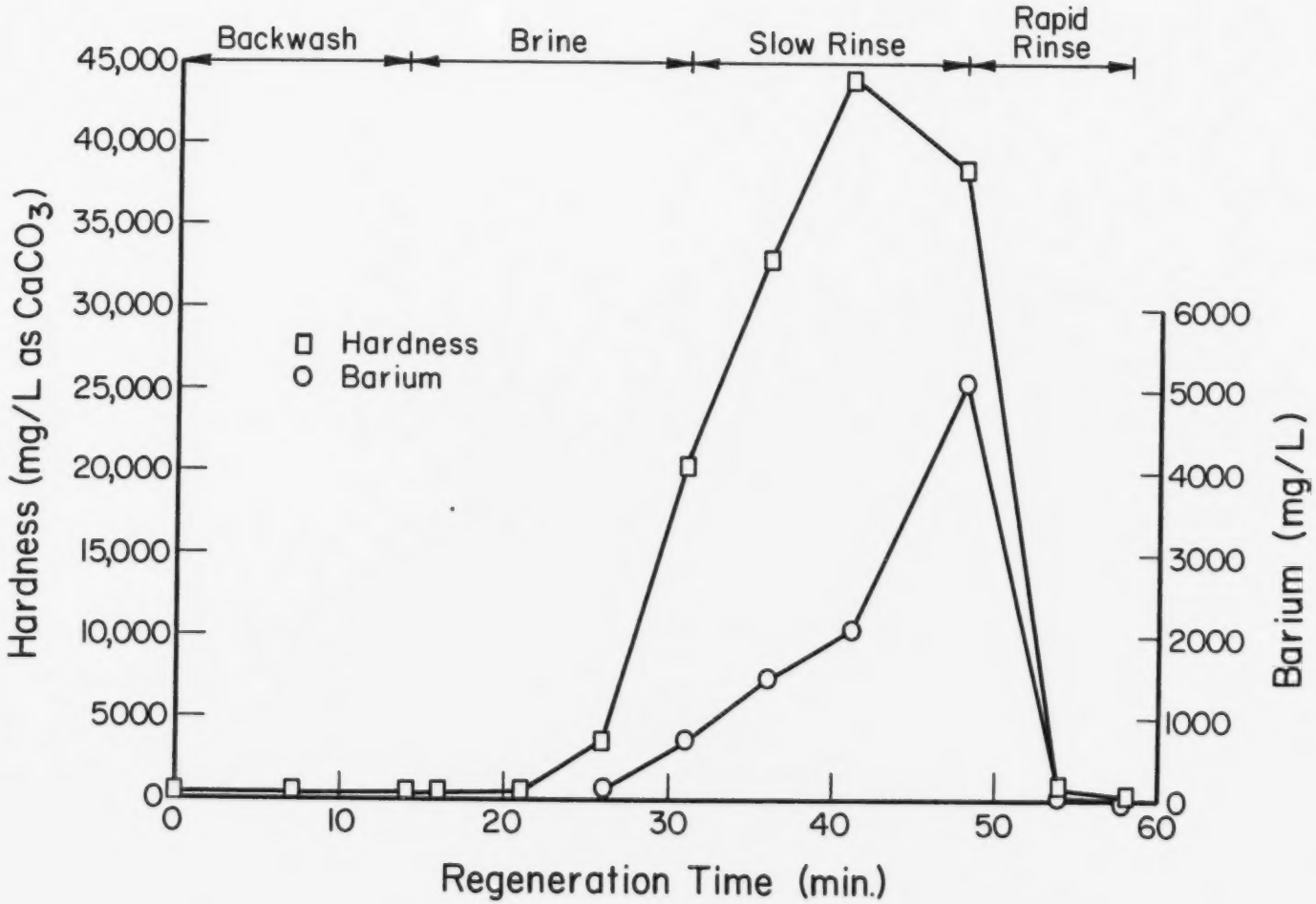

Figure 13. Barium and hardness concentrations in spent brine at Crystal Lake, IL, Well #8.

greater amount of the barium on the column before regeneration at Well #8 (78.4 g Ba/ft^3) compared to that at Well #6 (40.4 g Ba/ft^3). More barium accumulates on the resin during the service cycle at Well #8 because of a higher raw water barium concentration, and a lower regenerant dose applied to the column per unit volume of water processed during the service cycle (17).

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